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Flame synthesised vanadium and molybdenum oxide catalysts for oxidative dehydrogenation of propane

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Liquid fed flame spray pyrolysis (FSP) is a novel one-step synthesis method for preparation of nano-sized particles [1]. Organo-metallic compounds are dissolved in an organic solvent and the precursor solution is sprayed as micrometer sized droplets with high velocity oxygen and ignited with a small methane-oxygen flame [2]. The solvent and metal compounds evaporate and combust to form atomically dispersed vapours, which nucleate to form non-porous nanoparticles. The flame process gives high maximum temperature and a short residence time with thermally stable homogeneous nanoparticles as the product, which is ideal as heterogeneous catalyst. This study investigates supported vanadium and molybdenum oxide as catalysts for oxidative dehydrogenation of propane. The catalysts were used directly after synthesis by FSP without calcination or other processing steps.

Results

Alumina supported vanadium and molybdenum oxide, and mixed vanadium-molybdenum oxide catalysts were synthesized in one-step using FSP with transition metal loadings from 2 to 15 wt.%. The catalysts were investigated with TEM, XRD, BET and Raman spectroscopy. Specific surface areas from 140 to 170 m^2/g were obtained, corresponding to an equivalent spherical particle diameter of 9 to 11 nm, which was confirmed by TEM. XRD and Raman spectroscopy showed traces of crystalline bulk V_2O_5 or MoO_3 only at the highest loadings. The active phase is thus supported VO_x and MoO_x monomers or oligomers depending on the surface density, as observed with Raman spectroscopy.

The catalytic activity and selectivity for oxidative dehydrogenation of propane was investigated in a plug flow reactor (PFR) at different contact times and temperatures with a gas composition of $C_3H_8/O_2/N_2$ = 5/25/70. The products could be ascribed to a reaction network consisting of oxidative dehydrogenation of propane, parallel combustion of propane and consecutive combustion of propene [3]. The solutions to the design equation of a PFR for the conversion of propane and the yield of propene

were fitted to the experimental data to obtain the rate constants k_1, k_2 and k_3, assuming first order in propane and zeroth order in oxygen (Fig. 1) [3].

$$C_3H_8 + \frac{1}{2}O_2 \xrightarrow{k_1} C_3H_6 + H_2O$$

$$C_3H_8 + \left(2 + \frac{3}{2}x\right)O_2 \xrightarrow{k_2} 3CO_x + 4H_2O$$

$$C_3H_6 + \left(\frac{3}{2} + \frac{3}{2}x\right)O_2 \xrightarrow{k_3} 3CO_x + 3H_2O$$

$$X_{C_3H_8} = 1 - e^{-\frac{w}{F}(k_1+k_2)}$$

$$Y_{C_3H_6} = \frac{k_1}{k_3 - k_2 - k_1}\left(e^{-\frac{w}{F}(k_1+k_2)} - e^{-\frac{w}{F}k_3}\right)$$

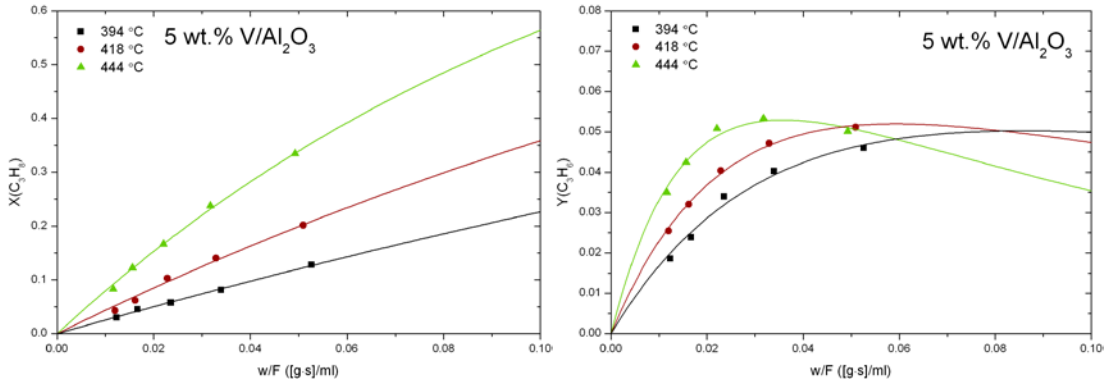

Fig. 1: Reaction network, PFR design equation solutions and measured conversion and yield for a 5 wt.% V/Al_2O_3 catalyst, with the solutions to the design equation fitted to the experimental data.

The reaction rate constants determined at temperatures from 380 to 500 °C enabled the determination of the apparent activation energy and the pre-exponential factor for the three reactions. This was used to predict the optimum reaction conditions for a high propene yield. The model was validated by comparing the predicted and the measured conversion and yield after increasing the temperature 80 °C and reducing contact time. The best catalysts were V/Al_2O_3 with 2 wt.% V, with a maximum propene yield of 12 % at 33 % propane conversion. For Mo based catalysts the best yield was obtained using high Mo loadings of 10 wt.% Mo, with a maximum propene yield of 9 % at 32 % propane conversion.

Conclusions

Supported vanadium and molybdenum oxide catalysts were successfully prepared by FSP. The catalysts were active in the oxidative dehydrogenation of propane, with a high propene yield for the vanadia based catalysts. The activity data could be interpreted in terms of a kinetic model which can predict the conversion and yield at different contact times and temperatures in a PFR.

[1] R. Strobel and S.E. Pratsinis, *J. Mater. Chem.* **17** (2007) 4743.

[2] L. Mädler, H.K. Kammler, R. Mueller, S.E. Pratsinis, *J. Aerosol Sci.* **33** (2002) 369.

[3] K. Chen, A. T. Bell, E. Iglesia, *J. Phys. Chem. B* **104** (2000) 1292.